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FUEL CELL STACKS

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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

Processes for the manufacture of phosphoric acid fuel cell components are described. Electrodes, matrices and bipolar gas distribution plates for use in fuel cells with an active area of approximately 0.4 sq. ft. is fabricated. Samples from these components have been tested in fuel cells and all items have demonstrated life in excess of 1000 hours. Performance data is given. Large component and stack testing will be initiated in the second report period.

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1.0 INTRODUCTION

During the first reporting period the majority of effort has been directed at translating technology for small component manufacture on a laboratory scale into large size components on a pilot plant production basis. The second major activity in this period was the laboratory testing of portions of these large components for performance and endurance.

The three main components undergoing scaleup and production study are the electrodes, matrix, and bipolar plate. Scaleup and production techniques for each of these items will be described separately. In this report the processes used to make the various components are only generally outlined. Specific operating conditions are still in a state of flux. More complete details will be presented in later reports when all manufacturing variables are fixed. A section on all test results will also be presented.

For each of the components mentioned above ERC has previous experience on both a small scale production and test basis with the exception of the bipolar plate with which only limited testing was done. As translation from this experience was made to larger components and from laboratory to production processes, it was necessary to make changes which could affect overall operating characteristics. In general minimal changes were made wherever possible but in some cases practical production methods or material availability necessitated significant changes. These changes and the reasons for them will be identified. In no instance have we seen any evidence that threatens to deny successful completion of the project as originally conceived.

2.0 MANUFACTURING METHODS

2.1 Electrodes

2.1.1 General Description

Electrodes for the ERC acid fuel cell stack consist of a two layer composite structure. The catalytically active portion consists of a layer of precious metal black catalyst bonded together with polytetrafluoroethylene (PTFE). For the anode catalyst a mixture of platinum black, rhodium black and tungsten oxide is used and for the cathode a mixture of platinum black and fine graphite is employed.

The catalyst layer is laminated with a graphite substrate or support layer made from a sized graphite and PTFE. The catalyst layers are nominally 2-3 mils thick and the support layer 10 mils thick. Each layer is manufactured separately and the two layers are then laminated together

under pressure and sintered. The sintering provides a bond between the PTFE in the two layers.

The specific manufacturing processes of the two layers are given below.

2.1.2 Catalyst Layer

The ERC electrode consists of 25% weight PTFE and 75% catalyst. Total catalyst loading is 2 mg/sq. cm. This low loading of high density catalyst materials represents too small a mass to be conveniently worked into a large cohesive uniform layer. To facilitate the even distribution of catalyst, a filler is added to the PTFE-catalyst mix. This filler is removed after the catalyst layer is fabricated.

In the original electrode process finely divided sugar was used as the filler material The sugar was removed by washing with hot water. This process while suitable for 2 in. x 2 in. electrodes did not readily translate into the 5 in. x 15 in. electrode required for the present program because of the difficulty in washing the large electrodes. Sugar was replaced by ammonium bicarbonate. The latter is removed by heating at 75C and is more amenable to production operation.

The electrode fabrication itself is otherwise similar to the process as originally contemplated. The catalyst layer is rolled on a calendering mill (Fig. 1) in strips 6 in. wide by 17 in. long. The extra size is to provide for shrinkage. The catalyst layer is dried to remove the Shell Sol rolling aid and the layer placed in contact with the support. The filler is removed and the composite structure is cut and laminated in a pressing mold shown in Figure 2. The final electrode is sintered in nitrogen at 340C and sized.

The overall process for the catalyst layer complete with production conditions is shown in Figure 3.

2.1.3 Substrate

The substrate is prepared by mixing PTFE powder and graphite powder, -100 +200 mesh, and rolling the graphite in the same calendering mill Figure 1 to a constant thickness of 10 mil. The substrate is dried to remove the Shell Sol. The substrate is now ready for lamination with the catalyst layer as described above. The overall electrode manufacturing process is shown in Figure 4.

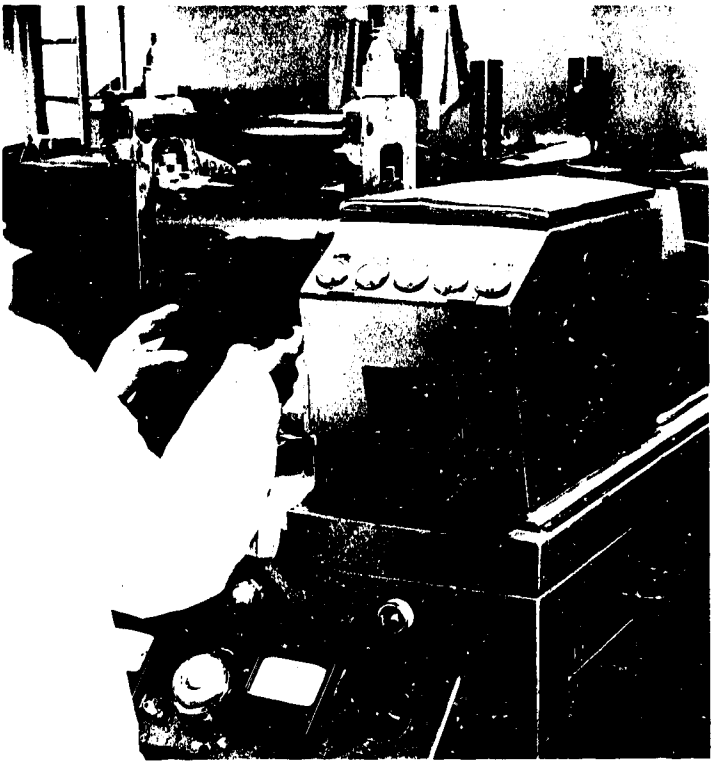


FIGURE 1 CALENDERING MILL

FIGURE 2 PRESSING MOLD

FIGURE 3 CATALYST LAYER PROCESS

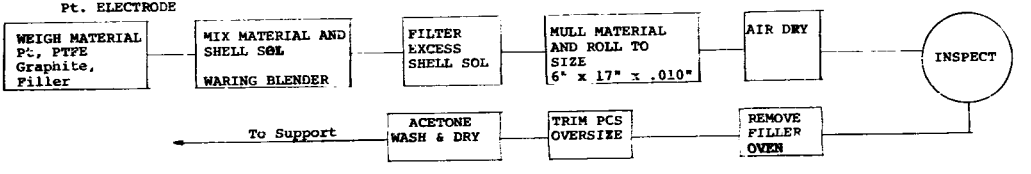
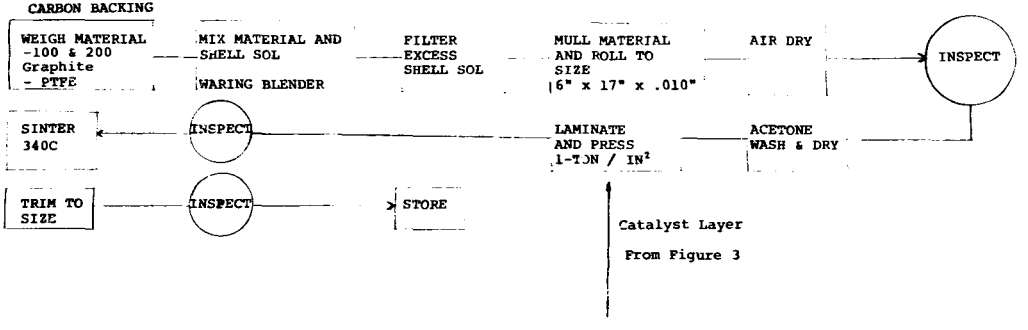


FIGURE 4 SUPPORT AND ELECTRODE PROCESS



2.2 Matrix

2.2.1 General

The matrix is made from a combination of Kynol fibers from the Carbonundum Co. and Resinox resin from Monsanto Corp. The overall process is one of paper making. The process was developed based on sheet molding. To fulfill the needs of the present project an 18 in. x 18 in. sheet-mold was ordered from Noble & Wood Corp. Although about a 2 months delay was encountered in delivery of this item it is now fully installed and operational. In the interim period, while waiting delivery of the larger mold our 12 in. x 12 in. mold was used to establish the manufacturing procedures for the process. About 2 dozen full size matrices have been fabricated successfully on the 18 in. x 18 in. equipment. One major difference in the process was caused by the fact that the original Resinox No. 674 was no longer manufactured by Monsanto. The 674 resin was a solid powder which we mixed with the fibers during processing. A chemically equivalent material Resinox 2279 is now made by Monsanto. The new material is in the form of an aqueous dispersion. This required several changes in our procedures. It appears, however, that the 2279 resin will result in a superior product once the new process described below is developed.

2.2.2 Process Description

The matrix manufacture can be conveniently divided into three separate processes as follows;

1. Fiber Digestion
2. Sheet Molding
3. Hot Pressing

2.2.2.1 Fiber Digestion

Fiber digestion consists of taking the as received fibers and treating them with hot concentrated phosphoric acid to enhance their wettability. The treated fibers are then washed to a neutral pH level and beaten to shorten the fiber length. A mixture consisting of 20% unbeaten and 80% beaten fibers is then used in the sheet molding step. The long fibers provide mechanical strength and the short fibers promote uniform density and facilitate molding.

2.2.2.2 Sheet Molding

The mixture of beaten and unbeaten fibers is mixed with deionized water in a blender at high speed to homogenize the mix. The Resinox 2279 is added to the fibers and mixing is continued for 3 minutes. At this point the blender speed is

reduced and 0.1N sulfuric acid is added to the mix. Sufficient acid is added to reduce the pH of the liquid to 4.5. The acid causes the binder to precipitate on the fibers. The total volume of the mix is now increased ten fold with water and poured into the sheet mold. Approximately 4 gallons of deionized water is added to the sheet mold while gently mixing the solution to prevent settling. At this point the sheet mold vacuum system is activated and the sheet is formed. Formation time with present equipment shown in Figure 5 is approximately 10 minutes. The vacuum system continues to run for 3 minutes after all the water is removed to enhance drying of the sheet. The sheet is now removed from the mold and air dried overnight. The dried sheet is now ready for the final hot pressing operation.

2.2.2.3 Hot Pressing

The final step in matrix manufacture is the hot pressing operation in which the Resinex is set and the matrix is finally sized with respect to thickness. The 18" x 18" sheet molded matrix is cut into three 6" x 18" pieces each piece is pressed to a constant thickness using 10 mil shims running along the 18" length of the piece. The pressing is done at 320F for 10 minutes. High production rates are most likely possible for these thin pieces. The sheet can be readily removed from the press without reducing press temperature enabling continuous operation of the heated press.

The overall process is shown in Figure 6.

2.3 Bipolar Plate

Bipolar plates are made in two steps. In the first step a 5" x 15" preform is manufactured. In the second step the preform is compression molded into the final shape.

2.3.1 Preforms

The manufacture of a preform with which to load the compression mold greatly simplifies the equipment needed for the molding operation.

The preform is fabricated wet by blending a mixture of Teflon, H-Resin* and graphite powder. The mixture is then fed to the same sheet mold used for the matrix fabrication. The preform is about 1 inch thick when removed from the sheet mold. Excess water is removed by pressing the preform at 200 tons in a hydraulic press (Figure 7). The preform now about one quarter inch thick is allowed to dry and is then ready for loading into the compression mold. Preforms in this state have some strength and can be readily

*Hercules, Inc.

FIGURE 5 18" x 18" SHEET MOLD

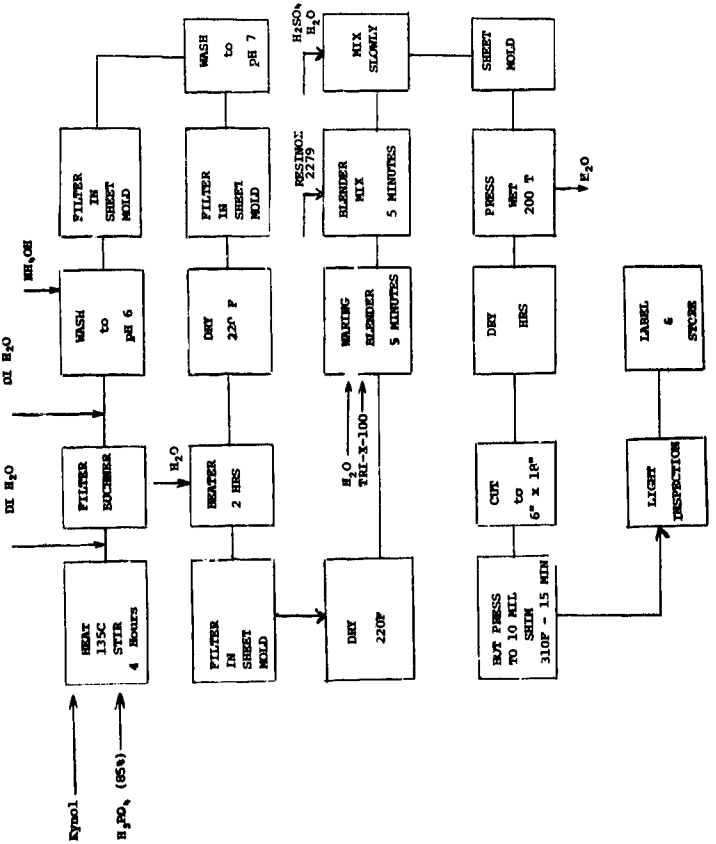


FIGURE 6 MATRIX PROCESS

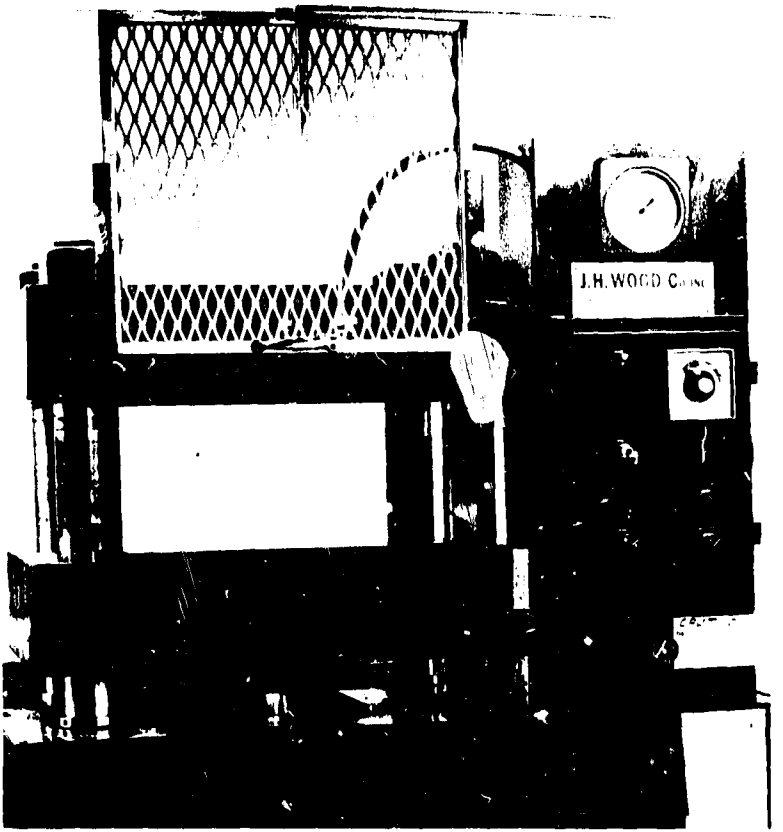


FIGURE 7 HYDRAULIC PRESS

handled or stored without breaking.

2.3.2 Compression Molding

A compression mold was designed to produce a complete bipolar plate in one operation. The finished plate would require no further machining other than two drill holes.

Molding parameters were determined by working with large 5" x 15" flat pieces. A molding pressure of 3000psi at 320F was found to yield close to a 100 percent dense plate.

The mold, made by an EDM machining process, includes a 7° taper on all groves and knockout pins along the anode chamber to facilitate release. Initial attempts at molding yielded some difficulties with the pieces releasing easily from the top platten (air side) but showing some inclination to stick in the mold cavity. The mold was slightly modified by the relocation of the knockout pins and the addition of a hydraulic system to lift the bottom platten out of the mold. The mold was also chrome plated. These relatively simple modifications permitted successful completion of the molding operation.

Sample pieces to test the mold were recently made. These are shown in Figure 8.

The overall process for manufacture of the bipolar plate is shown in Figure 9. Precise molding techniques are still in an evolutionary stage although no further mold modifications are anticipated.

The press with the compression mold in place is shown in Figure 10, and the compression mold itself is shown in Figure 11.

3.0 MATERIALS TESTING

3.1 General

Testing of components made by the production processes described earlier has been initiated. In all cases the testing has been conducted on small sections of the larger components because all of the large size components necessary to build large cells were not available.

Evaluations have been made in both fuel cells and in specific tests aimed at a particular characteristic such as porosity, conductivity, corrosion resistance, etc.

Tests have been conducted on electrodes, matrices, bipolar plates and seals. Initially fuel cell tests were conducted on only one item against standard components. Later as confidence was built several components were tested at one time. Major areas of testing are described below.

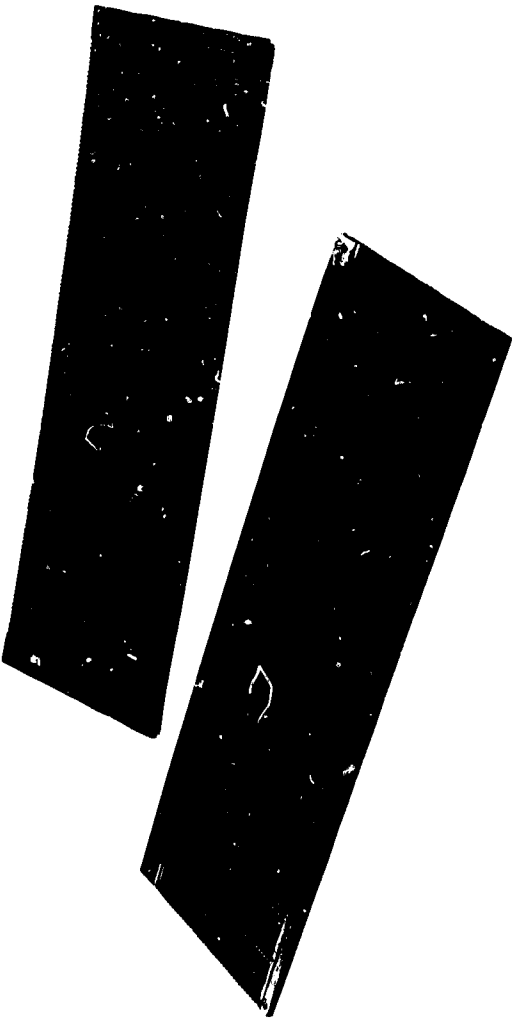


FIGURE 8

BIPOLAR PLATE

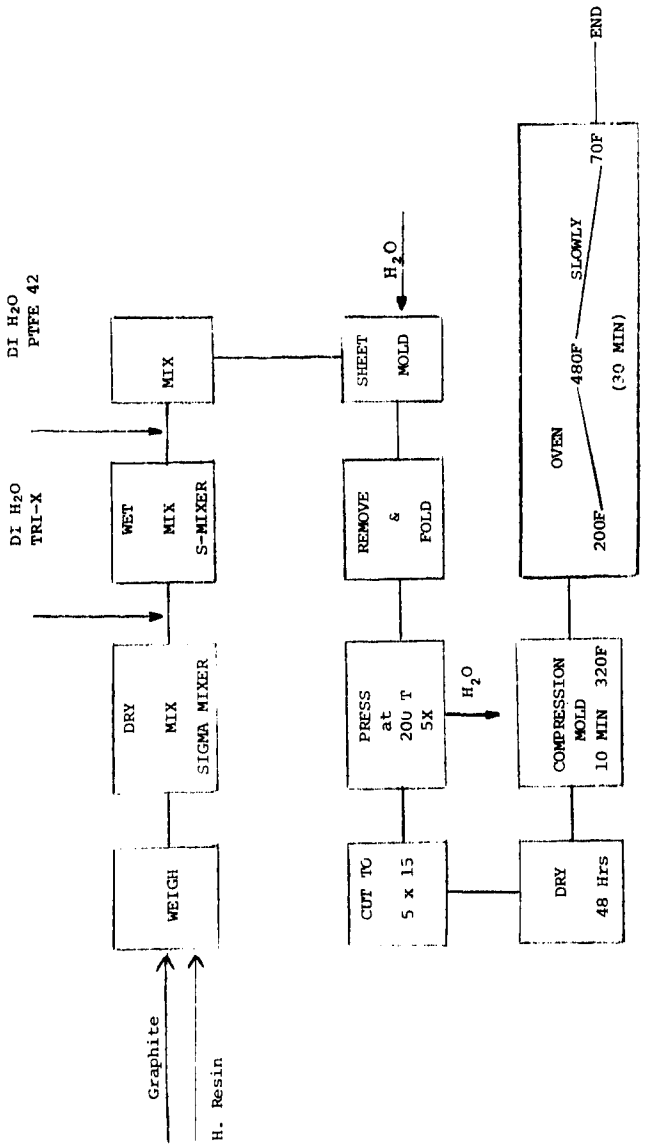


FIGURE 9 BIPOLAR PLATE PROCESS

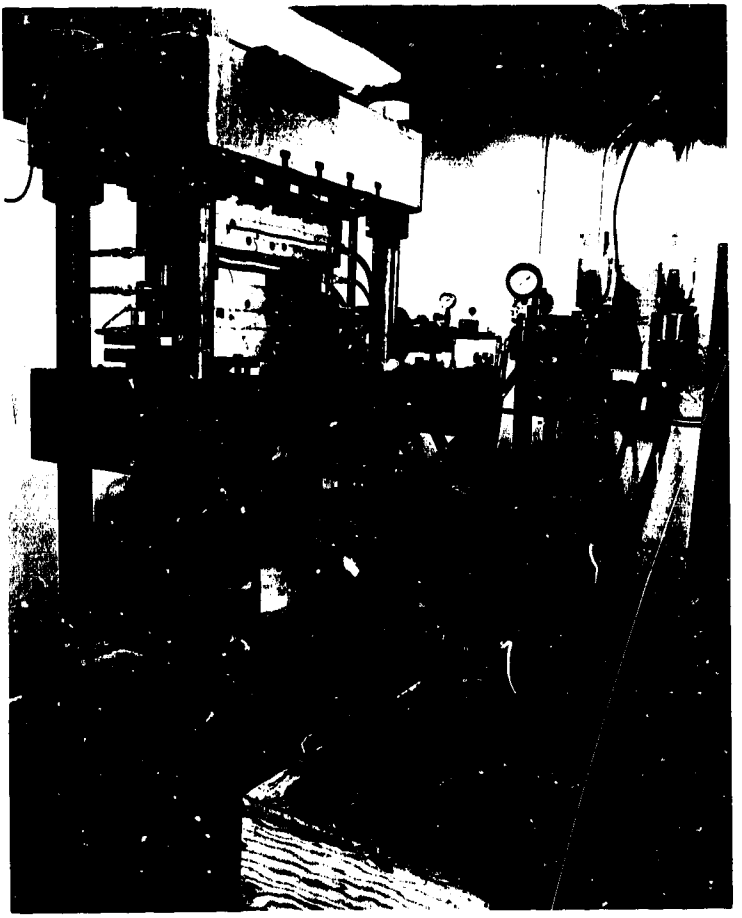


FIGURE 10 MOLDING PRESS

FIGURE 11 COMPRESSION MOLD

3.2 Electrodes

Large cathodes were made by the process described in section 2.1 and portions selected at random from the 5" x 15" electrodes were placed on test in 4 sq. in. tantalum test cells.

3.2.1 Air Electrode

Cathodes have been evaluated for periods of up to 1000 hours with standard matrices and screen type anodes against hydrogen. Cell potentials are constant at 0.57 to 0.58V at 100ASF. This voltage value is 70mV below that normally experienced. We believe that part of the loss is in the electrode since oxygen gains are running about 100 - 110 mV or about 30 mV higher than normal. The rest of the extra loss about 40-50 mV we believe to be in the relatively high resistance of the tantalum test hardware. Cell resistance losses are running close to 100 mV at 100 ASF and this value is about 50 mV higher than obtained in previous experiments. The extra loss in the electrode is probably due to the slightly higher density (lower porosity) of the machine-made electrodes. One major difference in manufacturing technique that could explain the 30 mV extra gain is the following. In Laboratory electrodes the catalyst layer was prepressed at 2500 psi prior to the final lamination to the substrate at 500 psi. Because the large 5" x 15" catalyst layers are difficult to handle, the lamination is done at higher pressure (2000 psi) and the separate catalyst layer compression is avoided. This higher pressure, one-step compression densifies the substrates by about 10% above earlier structures. The higher compression in the catalyst layer is needed in the ERC type electrode.

In an effort to raise performance of the electrodes, some were made with dispersed Teflon. These electrodes showed an initial performance of 0.6V at 100 ASF which dropped to 0.53V after 700 hours. Comparisons between the two types of electrodes are shown in Figures 12 and 13. Anode testing has only just begun as it was felt necessary to concentrate on the cathode and matrix structures.

3.3 Matrices

The matrix was the first component to be extensively tested. As indicated earlier we were concerned about using the dispersed form of the resin. Initial matrix testing was conducted with 10 mil thick matrices in a 4 sq. in. test cell. The matrix was tested for 1500 hours with standard screen electrodes on hydrogen and air. No performance degradation was seen as shown in Figure 14. Further there was no sign of cross gas leakage at the end of test. It was possible to stop the hydrogen fuel and pull a vacuum on the

FIGURE 18

ELECTRODE EVALUATION 2mA/cm² Pt ON GRAPHITE

TFE 42
280F 100ASF

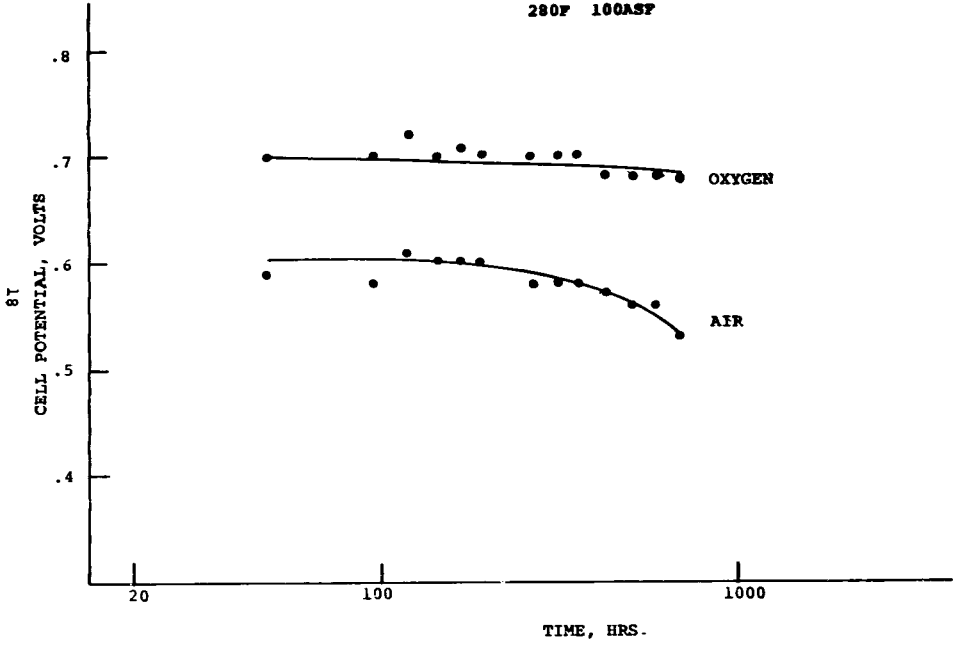


FIGURE 13

ELECTRODE EVALUATION 2mA/cm² Pt ON GRAPHITE

6C TEFLON
280F 100ASF

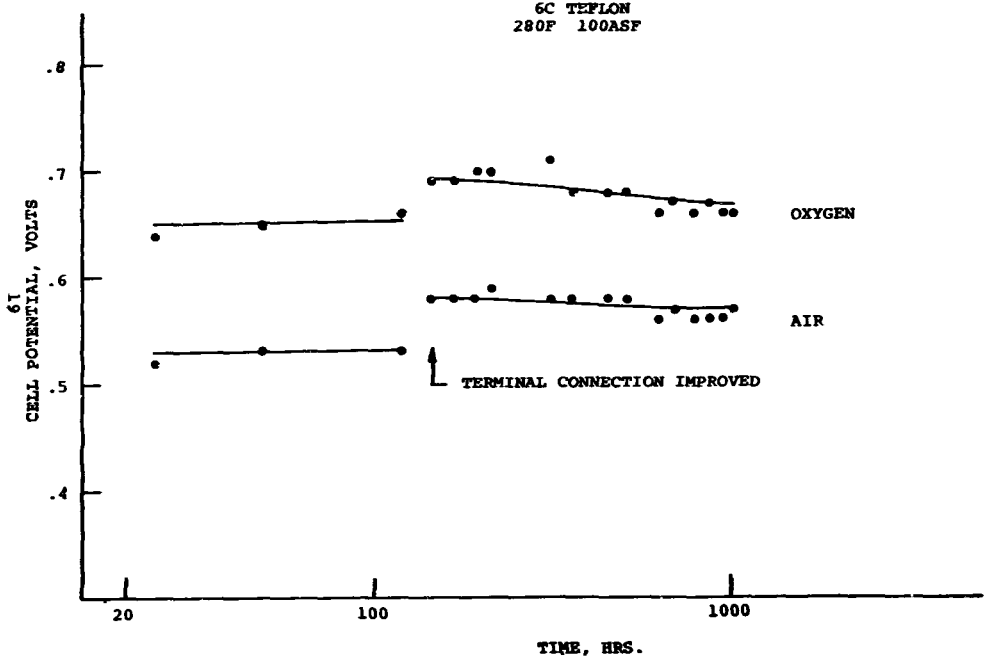
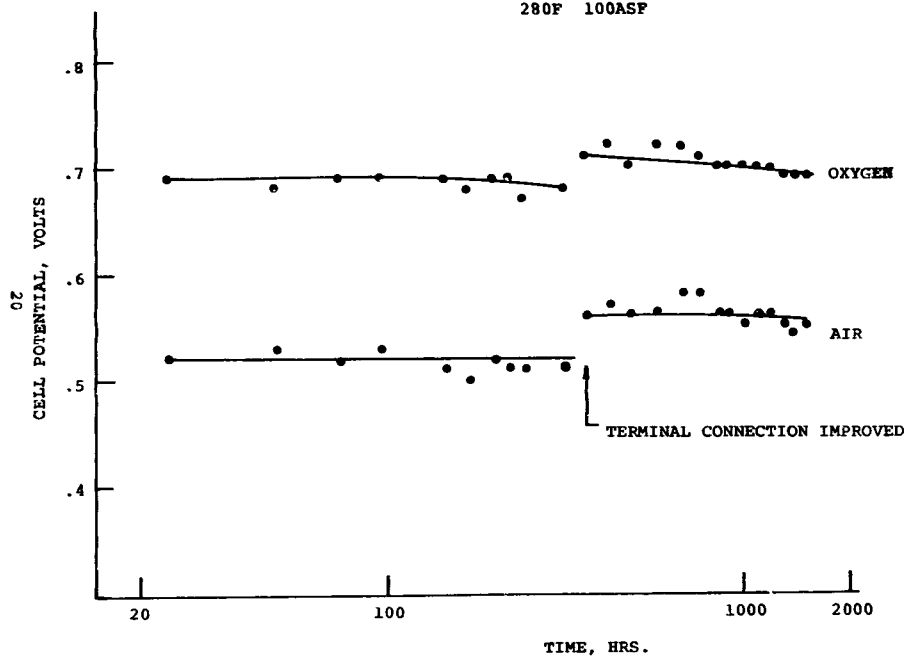


FIGURE 14

MATRIX EVALUATION TEST STANDARD ELECTRODES ON TO SCREEN

280F 100ASF



anode chamber as the hydrogen stored in the cavity was consumed. This technique is very sensitive for testing matrix leaks and is used continually in combination with OCV and gas flow sensitivity tests to detect leakage. This matrix design was fixed and used in other tests as a standard. Polarization curves for both electrodes and matrix after 500 hours are shown in Figure 15.

Recently a more porous matrix has been placed on test to improve conductivity. Cell resistance is considerably lower as expected but overall cell performance is the same. These data is not yet fully understood and additional tests are planned.

3.4 Bipolar Plates

Production of the bipolar plate requires the construction of a very sophisticated compression mold. The mold was only recently completed and full bipolar plates have not yet been manufactured.

While the mold was being fabricated passive corrosion tests were conducted by immersing sections of 5" x 15" flat plates made at ERC in hot phosphoric acid. Tests were conducted for periods of 60 days in 150C-100% H_3PO_4. No evidence of chemical attack on partially immersed specimens was seen. Independent density measurements showed that flat sheets could be fabricated with 100% apparent density. Specimens of these flat plates were machined into small cell housings with ribbed collection plates similar to those in the molded plates. Fuel cell testing has shown no evidence of attack on these plates at the operating potentials of the cells for test periods of 700 hrs.

Other sections of large plates were used to test sealing properties with seal materials.

Earlier work at ERC used polyphenylene sulfide resins in bipolar plates. This resin also showed excellent chemical properties but required higher temperatures to mold, 650-700F, than the H-Resin 320F. For this reason work on this program has been limited so far to H-Resin which can be molded more rapidly.

Characteristics of the H-Resin plates are shown in Tables 1 and 2.

The test rig developed for evaluating larger components is shown in Figure 16.

3.5 Seals

It is desirable to be able to seal the edge of the matrix

TABLE 1

CHARACTERISTICS OF BIPOLAR PLATES

A) POROSITY COMPOSITION	APPARENT DENSITY	THEORETICAL DENSITY	POROSITY
65% Graphite 840 32% H-Resin 3% TFE	1.64 9/cc	1.69	2.9
67% Graphite 840 33% Resinox	1.75	1.69	0
71.6% Graphite 840 25.1% H-Resin 3.3% TFE	1.81	1.78	0
76.5% Graphite 840 20.0% H-Resin 3.5% TFE	1.85	1.84	0
76.5% Graphite GP-38 20% H-Resin 3.5% TFE	1.86	1.84	0

TABLE 2

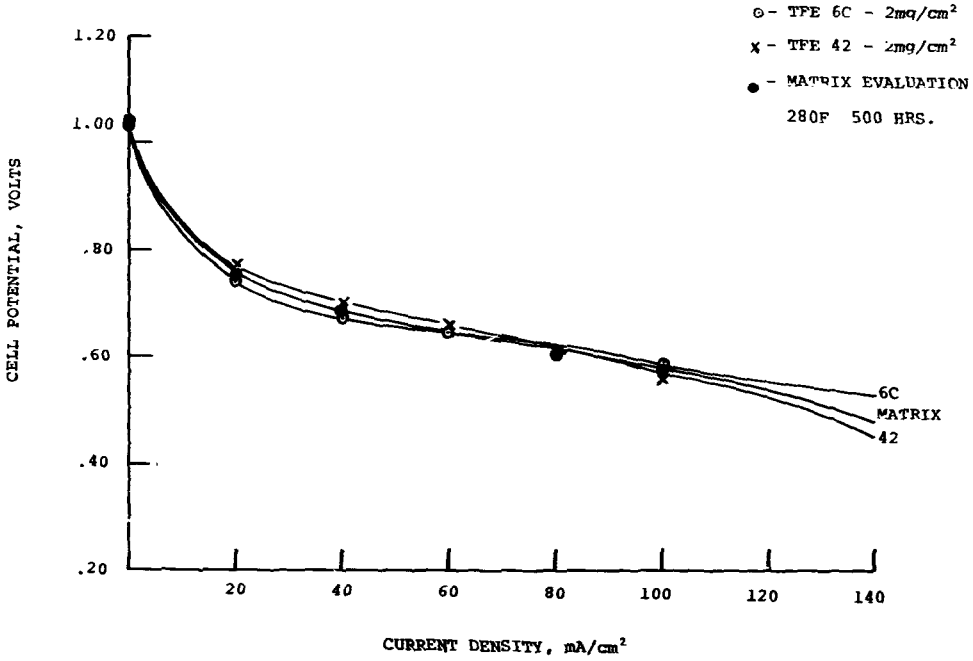
CHARACTERISTICS OF BIPOLAR PLATES

B) RESISTIVITY COMPOSITION	IN PLANE	THRU
65% Graphite 840 32% H-Resin 3% TFE	59.7×10^{-3} ohm cm.	
67% Graphite 840 33% Resinox	13.0×10^{-3} ohm cm.	
71.6% Graphite 840 25.1% H-Resin 3.3% TFE	26.7×10^{-3} ohm cm.	197×10^{-3} ohm cm.
76.5% Graphite 840 20.0% H-Resin 3.5% TFE	9.7×10^{-3} ohm cm.	99×10^{-3} ohm cm.
76.5% Graphite GP-38 20.0% H-Resin 3.5% TFE	106×10^{-3} ohm cm.	

FIGURE 15

POLARIZATION CURVES

2" x 2" SEGMENTS OF LARGE COMPONENTS



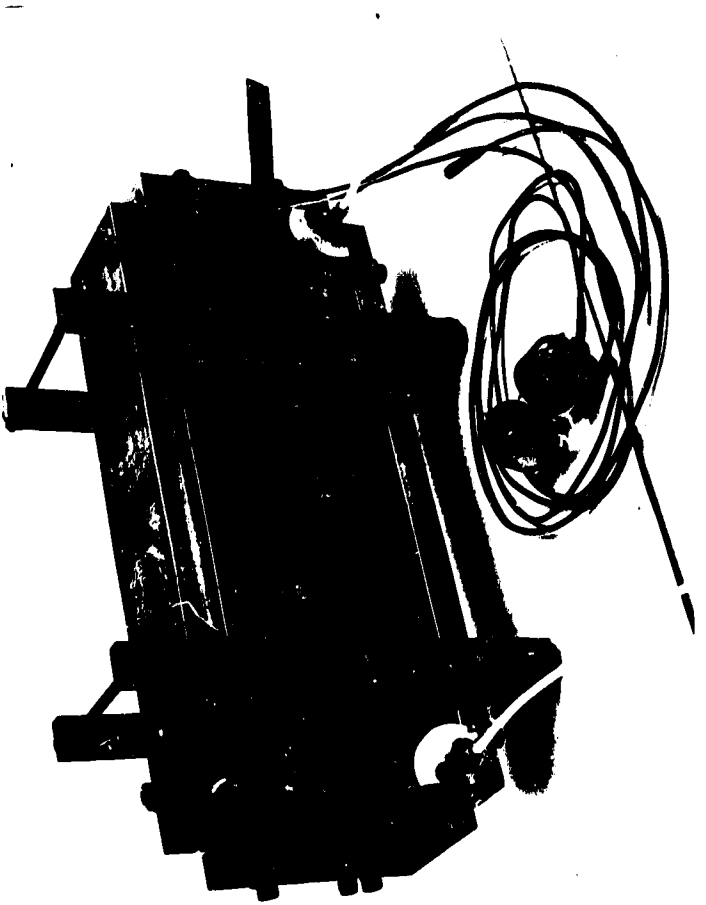


FIGURE 16

TEST RIG FOR 0.4 SQ. FT. FUEL CELL

to the bipolar plate to prevent gas leakage. The seals must be compatible with the environment. Several materials were tested by bonding together bipolar plate samples and placing them in 100% H_3PO_4 at 150C. Both Fluorel and Viton C-328 seals showed excellent bond strength after 30 days of testing. Viton C-328 was selected because of relative ease of application.

4.0 FUTURE WORK

In the next phase of the project the following tasks will be carried out.

1. Continued testing of components in 4 sq. in. test hardware.
2. Manufacture of bipolar plates by compression molding.
3. Endurance test large single cell components.
4. Assemble and test 10 cell stacks of large components.
5. Establish production rates for
    a. Bipolar plates
    b. Matrices
    c. Electrodes
    d. Stacks

5.0 CONCLUSIONS

Aside from some delays due to delivery of tooling, the project is proceeding satisfactorily. All components appear to have the basic endurance characteristics required for the program. Electrode performance is lower than anticipated but we believe it will be improved as the program progresses.

No major manufacturing difficulties have been encountered. All components can be made at reasonable production rates and unduly high manufacturing costs are not anticipated in any area.